Chapter 4

Informative potential of multiscale observations in archaeological biominerals down to the nanoscale.

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Abstract Humans have intentionally used biological materials such as bone, ivory and shells since prehistoric times due to their particular physical and chemical properties. The composite nature of biological materials at the nanoscale combined with an important structural hierarchy up to the macroscopic level is responsible for these exceptional properties. In this chapter we discuss the relation of the structural features of different biological materials within their archaeological and historical contexts along with their anthropological use and function. Amid the wealth of biological materials of archaeological interest, a special attention is paid to carbonate--based materials such as corals and shells and phosphate-based ones, including bone, teeth, ivory and antler. The structural features of these archaeobiominerals at different length scales down to the nanoscopic scale are highlighted in this chapter as they allow drawing conclusions on ancient working techniques, the provision and circulation of raw materials, anthropological heat processes, and, last but not least, on diagenetic changes and authentication purposes. The informative potential of observations of archaeological biological materials at different length scales is finally illustrated by some study cases.

1 Introduction

Biological materials are key witnesses of past societies, when they are preserved, as they serve as important archives in the archaeological and geological record bearing a wealth of information on ways of life, climates, environments and age in their shape, structure as well as in their chemical, isotopic and genetic composition. They have also been used to produce art objects from prehistoric to contemporary times because of their availability as well as the symbolic and precious nature of these materials. As such, those works of art convey information about technological skills and cognitive capabilities of human societies through the way they have been produced in relation to their specific chemical composition and structure (Backwell and d'Errico 2008; Backwell et al. 2008; d'Errico and Henshilwood 2007; White and Schwarcz 1989; White 1995, 2006; Conard 2003, 2009). Tracing the geographical origin of the artefact's material can also reveal trading routes and societal organizations of ancient cultures. Finally, the genetic analysis of these biological remains and artifacts can also shed light on the phylogeny and phylogeography of the respective animals which body parts are witnesses of past events (Nogués-Bravo et al. 2008; Haile et al. 2009; Enk et al. 2011).

Besides morphological and micro-morphological studies currently used in archaeology to investigate archaeological biological materials, an increasing number of physicochemical studies are dedicated to elucidate their structural, chemical and isotopic features (Weineretal.1998; Bocherensetal.2007; Buckleyetal.2008,2010; Zazzoetal.2006; Weiner and Bar-Yosef 1990; Bartsiokas and Middleton 1992).This adds a considerable amount of information contained in their hierarchical structure from the macro- down to the nanoscale. Up to the last two decades, biological materials were essentially studied using powdered samples,which,by destroying their hierarchical organization, resulted in a considerable loss of information. Therefore, many efforts were recently made to overcome this issue by improving the analytical procedures to obtain spatially resolved data on physical and virtual sections of these materials. At first, relatively small areas could be analyzed to establish elemental distribution profiles (e.g. Grime and Watt 1993; Reiche et al. 1999). Nowadays, two and sometimes three-dimensional (2D and 3D) elemental, molecular, structural and isotopic imaging of entire objects has becomes possible owing to recent technological developments off ocused analytical probes used in scanning mode and detectors (e.g. Lebon et al. 2011a; Reiche et al. 2011a, 2003, 2010; Reiche and Chalmin 2008; Anne et al. 2014; Bergmann et al. 2010; Gueriau et al. 2014; Gourrier et al. 2007b, 2010).

However, archaeological biological materials and objects are rarely preserved in their initial state and more likely modified in their constitution over time due to bio-physicochemical alteration processes also called diagenetic or taphonomic processes. These processes are complex because they are multi-factorial, non-linear in time and operate in a heterogeneous way and at different structural levels (Hedges 2002; Budd et al. 2000; Kohn et al. 1999; Reiche et al. 2002a, 2003; Dauphin and Williams 2004; Geigl 2002; O'Connor et al. 2011; Godfrey et al. 2002; Albéric et al. 2014; Large et al.

2011; Baud and Tochon-Danguy 1985; Jans et al. 2004; Nielsen-March and Hedges 1999; Nielsen-Marsh et al. 2007; Smith et al. 2007; Collins et al. 2002).

Diagenetic changes can bias the information yielded from archaeo-biominerals, such that it becomes important to distinguish features due to diagenetic changes from representative bio-physico-chemical markers of the past. This became particularly clear from palaeogenetic and palaeogenomic studies. Indeed, it is known that ancient DNA molecules are heavily fragmented and the nucleotide bases are chemically altered changing the genetic code (e.g. Pruvost et al. 2007, 2008; Llamas et al. 2012; Sawyer et al. 2012). For all those reasons, a precise evaluation of the informative potential of those archaeological witnesses of past societies remains a difficult challenge. However, much is yet to be gained from the study of objects made of biominerals, when considering carefully the morphological and biochemical signatures at the appropriate length scale with respect to diagenetic changes.

In this chapter, the informative potential of archaeological biominerals is discussed from a structural and morphological perspective at a very small length scale which forms what Steve Weiner introduced as "Microarchaeology", meaning, among other investigations, the study of the archeological information contained in the materials at the nano- and microscale which are not visible to the naked eye (Weiner 2010). For more in-depth discussions on biogeochemical signatures the reader is oriented towards other reviews and books such as *"Message d'os: archéométrie du squelette animal et humain"* (Balasse et al. 2015).

2 Structural and Chemical Characteristics of Some Biominerals of Archaeological Interest

The survival strategies of early human groups were based on exhaustive exploitation of surrounding materials. Beyond immediately available sources such as wood and stones, animals were also used extensively for their skins and fur as well as more rigid organs such as the skeletal parts and teeth. Therefore, in the archaeological context, especially the prehistoric one, the following biological materials are of utmost importance aside from wood, when preserved: bone, teeth, ivory, antler, skin, leather, hair, feathers as well as corals and shells. From this short-list, it can clearly be seen that biominerals occupy a central role.

Biominerals from marine or terrestrial origin, in their present form, are the result of an evolutionary adaptation process, which has persisted for millions of years. These materials are therefore considered to be well adapted to their respective physical and chemical environment (Weiner and Wagner 1998; Fratzl and Weinkammer 2007). This results in an amazing diversity of designs and shapes with characteristic functions. However, most biominerals essentially fall in three broad classes in terms of chemical composition: calcium carbonates (e.g. Shells, nacre), calcium phosphates (e.g. bone, teeth, woods) and silicates typically found in certain plants. Additionally, those materials are generally composite and exhibit a high degree of structural hierarchy at more than one length scale down to the nanoscale (Currey 2005; Lakes

1993; Addadi and Weiner 2001; Lowenstam and Weiner 1989; Mann and Weiner 1999).

Biominerals are often structurally optimized to achieve outstanding mechanical properties. Bone or shells, for example, combine a high stiffness and toughness, which are difficult to combine for most engineered bulk materials. Generally, stiff materials, like ceramics, are not very tough and, tough materials, like polymers, are not stiff. The combination of both classes of materials, (bio)minerals and (bio) polymers associated in varying amounts at the nanoscale to form (bio)composites allows combining those properties. The key for this efficient combination of mechanical properties in biomineralized tissues is their hierarchical structure (Fratzl 2004).

2.1 Phosphate-Based Biominerals

The phosphate phase generally found in biominerals is poorly crystalline carbonated calcium hydroxyapatite (a hydrated calcium phosphate). It is found among others in bone, antler, teeth and tusks (ivory). It is a very stable mineral and can accommodate many chemical species in its structure, which make it an ideal mineral for biologically controlled mineralization. In biominerals the nanocrystals of calcium apatite are generally embedded in a collagen-matrix. The imbrication of both phases is the key for the exceptional properties of these biominerals, some of them of archaeological relevance are discussed in detail in the following paragraphs.

2.1.1 Bone

Bones are extremely complex and smart objects (Fig. 1). First, because they are multi-functional as they must ensure body integrity and structure through the skeleton, thus protecting the most exposed organs (brain, heart, lungs etc.) and allowing movement through the musculo-skeletal system. Secondly, they host the production of red blood cells in the marrow around which bones form a sophisticated barrier. Third, they act as a reservoir for calcium storage, which is fundamental to all cellular processes throughout the body. Thus, the shapes, structures and chemical compositions of various types of bone must be seen as a reasonable compromise to achieve those three functions simultaneously (which implies that the mechanical properties should not be overestimated). Implicitly, this assumes that the bone shape/structure dictates the function (biomechanics) and/or vice versa (mechanobiology), i.e. the structure defines the function. We, now, have a very reasonable understanding that this is, in fact, the case (Currey 1999, 2002; Rho et al. 1998; Klein-Nulend et al. 2005; Carter and Beaupré 2007; Weiner and Wagner 1998).

Although the primary shapes of bones are encoded genetically and are determined during the first stages of growth (with many associated pathologies), the diet plays an important role in tissue formation and remodelling. The characteristic structural features of bone at microscale are the Haversian systems, also called secondary osteons (Fig. 2).

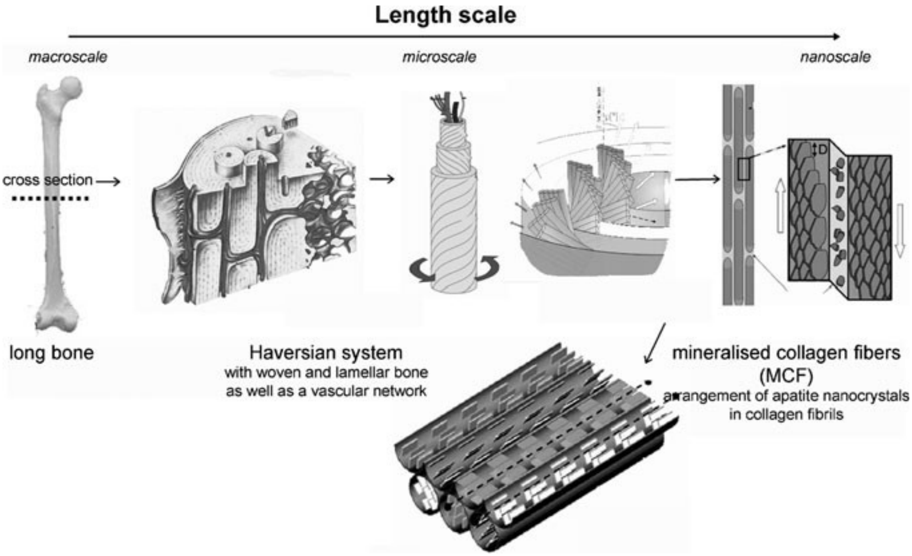

Figure 1 : Scheme of the structural hierarchy of bone. Adapted from Gupta et al. (2006), Rubin et al. (2005), Wagermaier et al. (2006)

The quality of the collagen and calcium phosphate, which constitutes the tissue will depend on the availability of calcium or similar types of ions and on the amount of amino acids present.

Collagen molecules are known to form a rather large family of ubiquitous macromolecules, which plays an important structural role in many different types of tissues including cornea, skin, artery, tendons, bone (Wess 2008). Depending on the tissue type and, thus, function, collagen molecules can form diverse supramolecular arrangements, from dense and rigid nano-/microfibrils to extended branched elastic networks. However, all collagen types share common characteristics (Hulmes 2008): they consist of three polypeptide chains, each of which having at least one domain formed by a repeating -(Gly-X-Y)-$_n$ motif, n generally falling in the range 337–343. The Glycine residue provides flexibility to the chains such that the overall macro-molecular conformation strongly relies on the nature of the two other amino acids and the extension of this domain. Ultimately, the presence of hydrophobic andhydrophilic residues results in a folding of the three chains in a right-handed triple helix, with the glycine residues positioned close to the central axis. In bone, collagen is of type I, and consists of ~ 20 % proline and hydroxyproline. The cyclic ring of these residues considerably limits the number of accessible conformations and provides rigidity to the molecule. The triple helix extends to ~ 300 nm in length and 1.5 nm in diameter and pack densely due to affinity between domains of adjacent molecules. This favors the formation of nanofibrils of ~ 100 nm in diameter, which are known to organize in different ways at the tissue (supra-fibrillar) level, from highly disorganized in woven bone, to cholesteric type packing in osteons, similar to synthetic liquid crystals. From this, it can be qualitatively understood that the resence (or absence) of specific vitamins in the diet can influence the physical properties of bone tissue, as has clearly been demonstrated for vitamins B, D and E (Arjmandi et al. 2002; Bailey and Wijngaarden 2015).

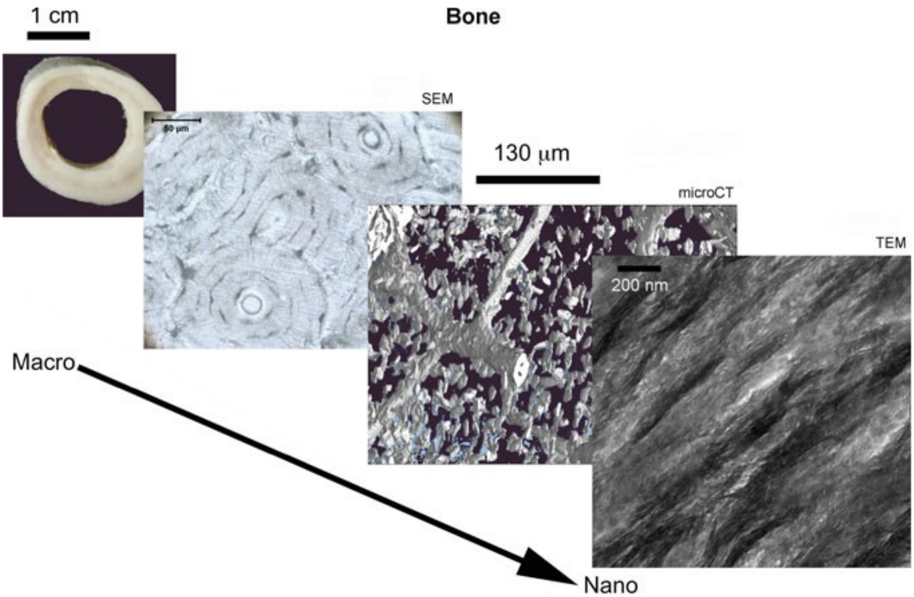

Figure 2 Structural features of bone observed at different length scales using optical, electron microscopy (SEM and TEM) and micro-X-ray tomography

The inorganic phase of bone (70 wt%) corresponds to a poorly crystalline carbonated hydroxyapatite with a chemical formula close to $Ca_{8.3}\square_{1.7}(PO_4)_{4.3}(HPO_4, CO_3)_{1.7}(OH)_{0.3}\square_{1.7}$ (carb. HAP) with a hexagonal crystal lattice ($P6_3/m$). In addition, bone contains about 10 wt% of water. Dietary factors can also affect the mineral composition in bone, which is generally found in the form of a carbonated hydroxyapatite (Posner 1969; Betts et al. 1981; Meneghini et al. 2003; Rey et al. 2009). It is, now, well known that bone mineral can accommodate various amounts of magnesium, sodium, fluorine, and even much heavier ions such as strontium or even uranium (Skinner 2013). Furthermore, a large number of crystal chemistry modifications can occur in bone, the most important one being carbonate to phosphate substitution. Such substitutions can have an important impact on the mineral crystal size, structure and organization at the nanoscale and can lead to drastic consequences for macroscopic scale properties (e.g. Boivin et al. 1988; Roschger et al. 1997; Rubin et al. 2003; Gourrier et al. 2010). In addition, the specific trace elemental composition of the mineral phase can be used to classify groups of individual and derive valuable archaeological information (Molleson 1987).

Of particular importance for studies based on the analysis of the mineral in bone artefacts is the isotope ratio composition, which has been shown to strongly relate to diet (Ambrose 1991; Balasse et al. 2001; Balasse and Tresset 2002; Bocherens et al. 1994, 2006; Ericson 1985; Iacumin et al. 1996; Lee-Thorp et al. 1997).

It is now well established that the mineral phase in bone forms as elongated thin platelet-shaped crystals with typical dimensions 3 × 50 × 100 nm 3 (Weiner and Traub 1986; Weiner and Wagner 1998; Rubin et al. 2003; Landis et al. 1996; Fratzl et al. 2004). These dimensions are very unusual when compared with geological apatite of similar composition. Additionally, the crystallographic c-axis has been shown to coincide with the main axis of the collagen fibrils within a couple of degrees at most (Wagermaier et al. 2013). As for other biominerals, these aspect can only be understood by taking into account the intimate relation between the two phases, the collagen fibrils serving as a template for mineral deposition and crystallization (Hodge and Petruska 1963; Landis et al. 1996; Traub et al. 1992; Weiner and Traub 1986; Ziv et al. 1996).

It is worthwhile emphasizing that any change from an average “reference” (healthy individual, animal) tissue structure should result in modifications of the collagen fibril/mineral nanocrystal structure and organization. In medicine, the nanoscale bone structure is currently investigated to evidence pathological modifications (e.g. Ruppel et al. 2008), while in archaeology and forensic sciences, this provides powerful markers of anthropological alterations or diagenetic processes (Chadefaux and Reiche 2009; Chadefaux et al. 2009b; Reiche et al. 2011a). Given that the archaeological bone artefact represents a structure “frozen” at a given time of life and setting aside the diagenetic modifications, one should thus be able to retrieve information concerning diet, ways of life and health of the indiviual by the thorough investigations of bones at all structural scales.

Additionally and, possibly, more importantly than the sole tissue composition, it is now a relatively well established fact that the structure of bone can be (strongly) affected by external stimuli such as mechanical loads. Thus, any kind of physical activity of an individual will trigger a cascade of cellular events leading to what is described in the literature as bone remodelling (as opposed to modelling, i.e. Bone formation) (Currey 2002). In brief, this implies resorption of damaged or unnecessary bone parts by osteoclasts and formation of new tissue by osteoblasts, e.g. To resorb micro-cracks, to better adapt to specific loading conditions etc. The magnitude of those cellular events is directly connected to the amount of external stimuli, i.e. an important physical activity will result in a higher remodelling. However, the remodelling activity can also be affected by various pathologies, osteoporosis being a well-known example.

2.1.2 Teeth

Teeth are specialized structures adapted for food mastication. Mammal's teeth present a wide range of morphologies depending of the phylogenetic groups, animal diets and functions (as for example in the case of proboscidian tusks). Teeth mainly consist of two parts: a crown and a root. The crown is generally coated with a hard layer called enamel, whereas the root, firmly fixed in the jaw, is coated with a tissue called cement. In many species, the crown enamel is also coated with cement. Underlying these surface layers, a resistant tissue called dentin forms the inner part and constitutes the "backbone" of the tooth. This dentin tissue is also the main constituent of tusks, where it is called ivory (because of its archaeological importance a special paragraph is dedicated to the description of ivory). Inside the tooth is the pulp, corresponding to a soft tissue including blood vessels and nerves.

Dentin of tooth and tusks is a composite material made up of an organic and inorganic fraction, which are intimately mixed on a nanometre scale. Dentin has basically the same composition as bone but differs in its tubular micromorphology due to a dentinogenesis starting by osteoblasts in the pulp. The organic phase of dentin (20 wt%) is mainly composed of a collagen type I matrix. The inorganic phase (about 70 wt%) consists, like in bone, of a poorly crystalline carb. HAP. In addition, they contain about 10 wt% of water. The organic matrix is first formed by odontoblasts and then mineralised during dentinogenesis. The mineralization continues with ages. The characteristic dentinal tubules radiate outward through the dentin from the pulp to the exterior cementum or enamel border.

Enamel at the tooth surface is the most highly mineralized and hard tissue of mammal. It is composed at 96 wt% by well-crystallized carb. HAP. This higher crystallinity is particularly due to lower amount of substituted carbonate (about 3 wt %) than in bone and dentin (up to 6 wt%). Organic matter (non-collagenous protein) represent less than 1 wt% and the rest is water (3 %). The enamel crystals can reach up to 1 μm length and 50 nm in diameter. The crystals are packed in small bundles called prisms around 4–12 μm wide and extended from the Enamel Dentin Junction (EDJ) up to the surface of the crown. The long axis of prism is perpendicular thus to the EDJ (Hillson 2009).

Because of its interesting mechanical properties, human tooth dentin has been studied to understand better the structure-mechanical function relations of mineralized collagen tissue. Wang and Weiner (1998) have shown that HAP are aligned in three dimensions within in individual collagen fibril and are found as aggregates without any preferred orientation leading to a anisotropic material regarding the structure (Wang and Weiner 1998). By testing the micro-hardness in the three orthogonal planes, they found that dentin is a mechanically isotropic material regarding the micro-hardness. This paradoxical situation was attributed to the variable modes of crystal orientation. More recently, Tesch et al. 2001 determined local variations of the mechanical properties by nano-indentation from the bulk dentin to the DEJ as well as in the size of particles (determined by small-angle X-ray scattering (SAXS) measurements) and mineralization degree (qBEI) (Tesch et al 2001).

The dentin layer close to the DEJ corresponds to a local minimum in hardness and modulus, which is known to stop crack propagation. This specific layer between enamel and bulk dentin has been characterized as a porous reticulate matrix of intertubular-dentin containing tubules with no peritubular dentin and presenting low stiffness. These specific properties are responsible for the durability of the whole tooth (Zaslansky et al. 2006).

2.1.3 Ivories

Ivory is generally associated with the dentin part of the exo-skeletal incisor teeth or tusks of several mammalian species, mainly elephant and mammoth (Laxodonta africana, Elephas maximus, Mammuthus) but also hippopotamus, warthog, walrus, sperm, killer and narwhal (Espinoza and Mann 1991). Teeth are specialized structures adapted for food mastication whereas tusks are mainly used for digging, foraging and as weapons. The study of the structure and composition of ivory is essential to understand the extraordinary mechanical properties required for the specific use of tusks.

From a macroscopic point of view, teeth and tusks have the same physical structures: the pulp cavity in the centre, surrounded by the dentin (main part), the cementum and a thin enamel layer at the outer surface. Two special kinds of macroscopic pattern can be observed in the dentin on tusk cross sections only for proboscidean ivory: the growth lines and the Schreger patterns. The growth line sequence, exploited using an isotopic analysis approach on micro-milled samples across the tusk, allow the determination of climatic variations, palaeodietary reconstructions and an estimation of the animal age (Codron et al. 2012; Fox and Fisher 2004; Fox et al. 2007). The elemental composition also varies significantly from the central tusk cavity to the cement layer of the tusk and variations in trace element concentrations (Mn, Zn, Sr) have been correlated to the growth lines in order to derive from it information on the environmental conditions during life time (Prozesky et al. 1995; Müller and Reiche 2011).

The Schreger pattern, firstly described as intersecting lines radiating in spiral fashion forming the Schreger angles (Miles et al. 1960), has been studied to distinguish between mammoth and elephant ivory and even between Asiatic and African elephant (Espinoza and Mann 1991; Singh et al. 2006; Trapani and Fisher 2003). The microstructural origin of the Schreger pattern is still not totally understood. Various microstructural models considering the arrangement, shape, distribution and orientation of dentinal tubules have been proposed. Considering the tubuli structure, the dentinal tubules are micro-canals that radiate outward through the dentin from the pulp cavity to the exterior cementum border. These canals are formed by odontoblasts that move centripetally in cytoplasmic filaments and depose dentin along their pathway. When the cytoplasmic filaments disappear they leave the dental tubules (between 0.8 and 2.2 μm in diameter) (Raubenheimer 1999). The 3D conformation of the dentinal tubules is under genetic control and therefore characteristic for the respective types of ivory.

According to Raubenheimer et al. 1998a, b), the Schreger pattern is the result of the sinusoidal and centripetal course followed by the dentinal tubule. However, Locke (2008) suggested that the tubules are not following a sinusoidal path but a straight one and the apparent sinusoidal curves are due to overlapping images in the helicoidal architecture (Locke 2008). Virag (2012) proposed a 3D model of the tubule organization for elephantoids introducing the “phase shift” model, which assumes a sinusoid undulation of the dentinal tubules in radial profile with different phases (Virag 2012). Recently, the work undertaken by Albéric et al. showed a helical tubule path combined with a phase shift (Albéric et al. accepted). Finally, Su and Cui (1999) explained the Schreger patterns from the collagen point of view. Collagen fibrils in ivory are in two radially distributed planes and interweave forming a network comparable to the rotated plywood structure observed in lamellar bone. The collagen fibrils form 2 μm large fibrils bundles lying parallel to one another within one layer and rotating by about 90° from one layer to its neighbour (Su and Cui 1999).

At the nanoscale, the average size of apatite crystals was determined to $31 \times 20 \times 3$ nm 3 . Jantou-Morris et al. (2010) published a “¼ stagger model” for mineralised collagen molecules analogously to the one proposed model for bones by Jäger and Fratzl (2000) (Jantou-Morris et al. 2010; Jäger and Fratzl 2000). The specific relationship between collagen fibrils and minerals give particular mechanical properties to the material. Ivory dentin is rich in Mg in comparison to other tooth dentin (about 6 wt%) and the Mg, being a key component for the stabilization of amorphous carbonate, is supposed to play an important role in biomineralization. Hence, several studies have been focused on this subject (Finch and Allison 2007; Politi et al. 2010).

Tusks, mainly used for digging, foraging and as weapons, are subjected to important compression and shear forces and present strong macroscopic mechanical anisotropy. Dentin is known to be stiff because of its mineral part and tough because of its organic part (Baohua and Gao 2004). Cui et al. (1994) investigated the orientation dependence of indentation morphology and micro-hardness of ivory (Cui et al. 1994). Nothnagel et al. (1996) correlated the texture of hydroxyapatite and mechanical properties related to the function of the tusk (Nothnagel et al. 1996). The correlation between the orientation of the collagen fibers and the elastic properties was shown by Nalla et al. (2003) for elephant ivory and by Currey et al. (1994) for narwhal ivory (Nalla 2003; Currey et al. 1994).

2.1.4 Antler

Antlers are bony appendages which are developed pairwise externally onto the frontal bone of the skull in most members of the deer family (Cervidae). They are made solely of bone tissue unlike keratin-covered horns (Chapman 1981). Similar to other bones they are composed of protein (mainly collagen type I), mineral (carbonated hydroxyapatite) and water. Their apatite weight content, however, is slightly less than that of bone which is why their elastic mechanical properties such as the Young’s modulus and, hence, the stiffness is lower than in bone.

The basic structure of antlers is similar to long bones, comprised of an outer compact bone shell enclosing a core of spongy bone. Antlers, however, stand apart from other vertebrate biomineralized organs. They are totally regenerated annually at a rapid growth rate. Although they grow over a very short period of time (4– 5 months), they can attain elaborate branched or palmate forms, huge sizes (>1 m), and weights of several kilograms. The microstructural arrangements that are important to such rapid and large-scale tissue growth and organization are, still, poorly known, although several studies of antler regeneration histogenesis have been performed (Banks 1974; Wislocki 1942; Kierdorf et al. 1995; Li et al. 2005). The characterization of the three-dimensional microstructural development in antler bone revealed that antler re-growth is a process of scaffold generation, replacement and then filling. The process begins with the building of a mineralized cartilage scaffold, composed of longitudinally oriented cartilaginous tubes of several millimetres in length. A lamellar bone scaffold, consisting of highly longitudinal oriented fenestrated bone tubes, then replaces the cartilaginous framework. In mature antler these bone tubes are then filled with primary osteons, leading to a pattern of less mineralized osteons situated within a more highly mineralized bone matrix (Krauss et al. 2011).

The most distinctive feature of antlers with respect to other bones is their remarkable toughness (Zioupos et al. 1994; Currey 1999; Launey et al. 2010; Rajaram and Ramanathan 1982). Structural toughening mechanisms at the micrometre scale such as microcracking, crack deflection, crack bridging, visco-plastic flow and combinations of these have been identified for bone (Launey et al. 2010; Zioupos et al. 1996; Nalla et al. 2003; Nalla 2005; Vashishth et al. 1997, 2000, 2003). Evidence was also found for a toughening mechanism at the nanoscale in antler compact bone. Results showed a heterogeneous response to load in antler after the onset of inelastic deformation. This was interpreted by the formation of isolated nanoscale defects, which clearly contribute to the antler's toughness (Krauss et al. 2009).

2.2 Carbonate-Based Biominerals

Calcium carbonate exists in three polymorphous forms: calcite, aragonite and vaterite, two of which namely aragonite and calcite are found to be the major phases in carbonate-based biominerals such as shells and corals. Calcite is the thermodynamically more stable phase under ambient conditions. It crystallizes in a rhombohedral lattice system and is pure of a whitish colour. Aragonite is the more stable polymorph under high pressure and crystallzes in a orthorhombic lattice system. It is less frequent than calcite in nature and also shows a white colour.

2.2.1 Shells

Shells are the result of a biologically controlled process of shelled molluscs. Shelled molluscs can live in sea and in freshwater. The shell is formed by an anatomical part of the mollusc called mantle due to the super-saturation of calcium and bicarbonate.

Therefore, it is generally a calcareous exoskeleton with an organic calcifying matrix composed of a complex mixture of proteins, glycoproteins, polysaccharides, acids and chitine, which protects the molluscs including snails, clams, tusk shells etc. The organic matrix is genetically encoded to execute the assemblage of the shell. In general the shell is constituted of at least three morphologically different layers from the external border to the internal one: the periostracum (organic layer), one chalk-like prismatic layer (calcerous prismes) and an inner pearly, nacreous layer composed of lamellar successive calcium carbonate layers with organic substances. In general the calcium carbonate fraction represents 95–99 wt% of the shell and the organic matrix the remaining part of 1–5 wt%.

2.2.2 Corals

Corals are sessile animals having a polyp as body unit. They live mostly in colonies that gradually develop from a small start. Corals can be divided in stony and soft corals. Stony corals, also called hard corals, are of interest in the archaeological context as they are used as jewellery. Their skeleton is composed of calcium carbonate that provides hardness, strength and protection to the organism. The polyps are situated in cup-shaped depressions in the skeleton known as corallites.Stony corals can have very variable appearances as a function of different types of habitat, light levels and water movement.

Red coral, Corallium rubrum, is the most emblematic species used for jewellery and found in the Mediterranean Sea in depths ranging from 10 to 200 m. It is composed of a solid axial skeleton coated with living tissue. The cellular layer called ectoderm forms the external surface above a thick a cellular layer composed of collagen (mesoglea).This mesoglae contains small granules of living tissue also called sclerites. The mineral phase of the axial skeletal structures and the sclerites is composed of Mg-rich calcite. This biological calcite also contain about 1.5 wt% of organic matter. The color of red corals is attibuted to the presence of conjugated hydrocarbon chains, whose structure and chain length is still the object of controversy. The crystals are arranged in submicrometer crystalline units. These units show different crystal sizes and shapes although platelet-like crystals are predominant. Their size varies between some tens to some hundreds of nanometers(Vielzeufetal.2008). Further transmission electron microscopy (TEM) observations revealed the presence 2–5 nm crystal domains in the submicrometer units that are actually composed of 50–100 nm crytalline superstructures. These formations have important implications for the mechanisms of crystal growth in the living organisms. Interestingly such nanocomposite structures are common to many biominerals. A long-range crystallographic order combined with interfaces at various scales might be responsible the various shapes observed of this kind of biominerals (Vielzeuf et al. 2010). The growth rings of corals are marked by a variation in the Mg and the organic matter content. These variations are anti-correlated and can be used for chronological issues as annual variations have been reported. All these features can be exploited for archaeological, environmental, climatic and geological issues.

Figure 3 Example of an archaeological object dating from the Iron Age bearing an altered red coral from the Celtic princely tomb of Asperg-Grafenbühl, Baden-Württemberg, Germany

There has been research on red corals for 130 years (Tischler 1886; Olhausen 1888), but there have been hardly any extensive studies on archaeological findings (Fig. 3) (Perrin 1996; Liverino 1989; Tescione 1965). One reason for this limited research is possibly that corals lose their intense red colour and shiny surface structure due to poorly understood ageing processes, which is why other light-coloured materials such as bone, ivory, chalk or shells are often mistaken for corals.It is therefore not surprising that attempts have repeatedly been made to identify these substances in archaeological contexts using different methods (Fürst et al. 2014).

3 Archaeological Implications of the Study of Biominerals

As already stated, biominerals are an important source of raw material used by former human societies. Therefore, these materials can be used as tracers for provenance and circulation studies of these materials, when their exact nature is well characterized. They can give insights as worked objects onto ancient working techniques of the material (bone, ivory, antler) to be used for tools and weapons as well as on production processes for art objects. In many cases these objects were heated, especially in prehistoric times. Information on former production techniques can also be inferred from the study of heat-induced transformations of these materials. As biological materials, these objects can be used for multiple dating purposes, diet reconstructions as well as environmental and climatic studies (Fig. 4). The latter types of information are generally inferred from stable or instable isotope analyses and not from structural features, except in the case of the study of microwears on teeth. Therefore these isotopic studies are not discussed in this chapter and the reader can find information on this elsewhere (Balasse et al. 2015; Bocherens et al. 2006; Dupont and Marchand 2008; Gillespie et al. 1984; Hameau et al. 2007; Hedges and Law 1989; Latham 1997; Millard and Pike 1999; Rink et al. 1996; Saliège et al. 1995).

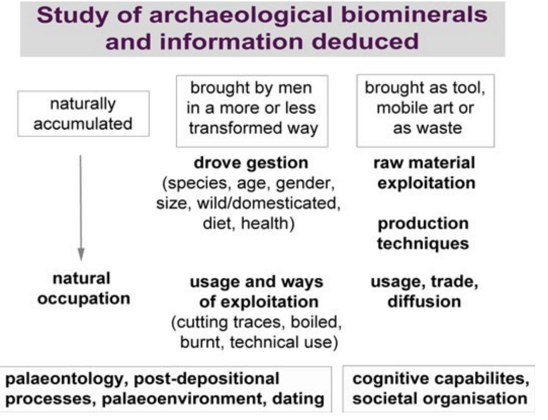

Figure 4 Overview of the possible implications of the study of archaeological biominerals (pers. comm. M. Regert)

3.1 Tracers of Provenance and Circulation

The study of the provenance and circulation of biominerals in the past is important because these materials have been widely used by ancient societies as tools and as art objects (e.g. body ornaments). The study of tools and art objects is not only interesting to get insights into working techniques, cognitive capabilities of the humans but also because they can be used as tracers of social and technological exchanges between civilisations.

Due to the wide distribution of archaeological biomineral finds, distinct types of social activities can be addressed. If an economically-oriented perspective is considered, three functionally and geographically distinct areas can be differentiated: (1) a production zone, (2) a trading zone and (3) a consumption zone. A special attention concerning provenancing and circulation studies is paid to precious biominerals such as ivory and corals used to produce different kinds of art objects. As a prominent example, elephant ivory has been traded between Asia, Africa and Europe. As shown in ancient times the geographical areas, where the animals (elephants and mammoths) lived, and the cultural regions, where the material was used, do not necessarily coincide. Therefore, the study of the spread and commercialization of ivory with respect to its biological origin can provide valuable information about exchanges in ancient societies (Caubetand Gaborit-Chopin2004).

As another example, coral finds play a crucial role in the reconstruction of social structures, because they are present in many graves, wealthy or not, as well as in élite burials. The distribution of coral seems to show the coupling of coral redistribution with the local élites. In the late Hallstatt and early La Tène periods (620–250 av. Chr.), which are particularly rich in coral imports, they represent the most common Mediterranean find category. They are particularly well suited to understand the economic exchanges between Central Europe and Mediterranean cultures (Fürst et al. 2014).

Although there are legitimate doubts about the reliability of previous material interpretations, it can be assumed that a large number of objects have been incorrectly identified and the number of coral decorations actually present is much underestimated. Therefore, based on reliable materials identification, the informative potential of archaeological coral finds can be better exploited and their spread and trade studied in a more reliable way.

3.2 Working Techniques

Since Prehistoric times, the survival and acquisition strategies of human groups imply the use of animals in every respect. They provide nutritional resources and are an important source of raw material for the production of objects. The hard animal materials, above all osseous materials, were used to produce different kinds of equipment for "artistic" purposes such as statuettes and body ornaments as well for hunting such as projectile points. The different kinds of objects, their production techniques, functions and use are directly dependent on the specific morphological and mechanical properties of the different hard biological materials (Christensen 2004; Tejero et al. 2012; Christensen and Tejero 2015). The understanding and interpretation of these osseous objects therefore necessarily passes through the analyses of macro-, micro- and nanoscopic features of the used raw material in relation to the investigation of their mechanical properties to check the adequacy of the relationship between structure, function and use. Sometimes when the artefacts are heavily carved, the type of osseous material or the type of coral is difficult to be determined. In these cases physico-chemical analysis and morphological studies at different length scales are of outmost importance to identify the employed biological material. The size and morphology of biominerals—combined with other critical factors like mechanical properties, availability as well as a conceptual vision of each animal—have certainly influenced the choice of prehistoric and historic craftsmen in their quest for functionally adapted blanks to produce the artefacts. For example, bones with broad surface would be adequate to receive regular decorative feature such as the ribs of medium or large herbivores. Antlers of deer, because of their exceptional stiff- and toughness, provide the functional requirements necessary for a large part of prehistoric hunting equipment (projectile points).

Ivory, a tough and durable material coming from the tusks of strong animals such as mammoths and elephants, adds a high symbolic value to this material within Prehistoric and historic societies. It can be related to wood as it is large enough to be carved and sculptured in different ways without inflicting, as other bone materials, its original macroscopic form. Ivory seems to be the preferred choice to produce art objects, statuettes and personal ornaments (Fig. 5). In later time, ivory was also used in combination with other valuable materials, such as gold and pigments (White 1995). Materials characteristics including their mechanical properties, colour, shape and use wear are important clues to confirm hypotheses about the use and symbolic function of valuable objects (Christensen and Tejero 2015).

Figure 5 Phoenician ivory carving "Woman at the window" (Inv. No. AO 11459) from Arslan Tash site, Syria, 8th c. BC, kept in the collection of the Département des Antiquités Orientales of the Louvre museum, Paris

3.3 Heat-Induced Transformations

Biominerals can be used as combustible because they contain organic substances. Indeed, traces of heating are often observed on bone fragments and artefacts in the form of color changes and increased mechanical fragility (Stiner et al. 1995; Shahack-Gross et al. 1997; Weiner et al. 1998; Reiche 2009b; Chadefaux et al. 2009b). The way offiring and the firing temperature can allow drawing conclusions on management of resources in former societies. In many cases, however, the effects on bone are difficult to distinguish from other diagenetic phenomena, which could induce similar changes (Bennett 1999; Reiche et al. 2000, 2002b). In some cases, they are identified as burned on the basis of the context in which they are found on the field (e.g. urns), despite of the absence of any colour changes.

This often leaves unanswered a number of questions relating to the identification, conservation and understanding of the accidental or intentional origins of the heating process (Koon et al. 2003, 2010).

3.4 Microwear Studies

Besides personal body ornaments, bones, teeth and even shells are important nutritional resources, providing indications of ways of life. They also represent important archives of information from their macroscopic and microscopic properties, up to their elemental or isotopic composition (Tütken and Vennemann

2011). Palaeontologists usually used teeth morphology or dental microwears to obtain palaeodietary information of animal or human extinct species. Enamel growth marks and other histological features can be used to reconstruct the life history of animal or human fossil specimens (e.g. timing of tooth development, weaning and feeding stresses). Teeth and bone morphology can be used to reconstruct phylogenetic relations between species, especially for human remains.

4 Diagenesis and Taphonomy of Biominerals

Diagenetic and taphonomoic processes of archaeological biominerals are very complex as they are multifactorial and non-linear in time (Fig. 6). They occur during burial time and depend, among others, on material properties (type of tissues, bone, teeth morphology, age of specimen, etc.). They are controlled by external factor such as microorganism development and physicochemical conditions in the burial environment (temperature, moisture, pH, redox condition) (Nielsen-Marsh et al. 2007; Smith et al. 2007; Hedges 2002; Collins et al. 2002). Although osseous and shell remains constitute the most resistant skeletal remains, they can undergo significant modifications of their structure and morphology after the death of the individual. The most important processes are induced by climatic (weathering) and edaphic conditions, such as temperature and moisture variations which induce a fracturation, similarly to compaction in sediment (Hedges 2002; Denys and Patou-Methis 2014).

Different post-mortem processes can deeply affect histology, micro-structure, mineralogical properties and composition of these tissues. These processes occur even before burial, since microbial organism (bacteria and fungi) can colonize organic-containing tissues as soon as the first steps of flesh putrefaction. Microbial development results in alterations of histological micro-structures. Collagen loss in phosphate-based biominerals leads to an increase of porosity that, in turn, modifies the possibility of exchange between mineral phase and surrounding sedimentary environment during burial (Collins et al. 2002). Alteration processes can induce dissolution and/or recrystallization of the biomineral in more thermodynamically stable phases (more stoichiometric carbonate apatite, HAP and finally fluroapatite for phosphate-based biominerals and in calcite for carbonate-based minerals) and the precipitation of authigenic minerals in porosities (Berna et al. 2004; Kohn et al. 1999). Dissolution-recrystallization processes or diffusion, absorption and ionic exchange processes can promote the incorporation of foreign ions in the crystal lattices.

Some of these alteration processes can lead to a preservation of biomolecular proxies or appearance of geochemical signals. Re-crystallization of biogenic biominerals during the first steps of diagenesis can encapsulate non-collagenous proteins or DNA fragments within crystal aggregates and preserve them to long-term alteration.

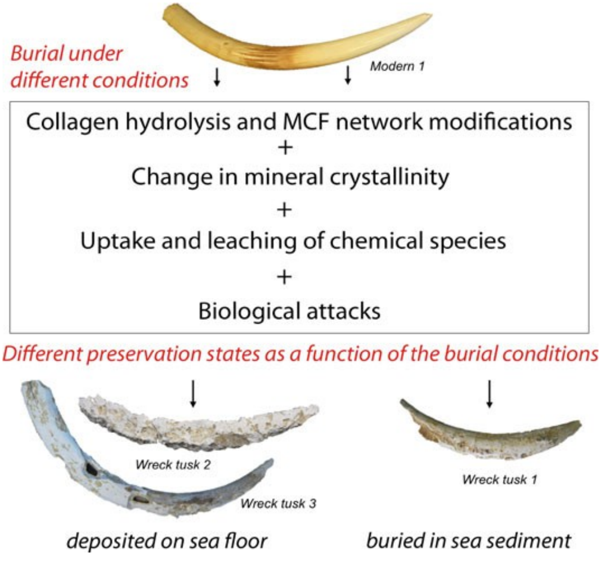

Figure 6 Example of early diagenetic processes of elephant ivory from a marine site Les Poulins, Brittany, France. Adapted from Albéric et al. (2014)

Uranium uptake in dental, osseous and calcareous material and accumulation of electrons in paramagnetic centres of apatite crystal lattice over geological time can allow obtaining chronological data by Uranium-series and Electron Spin Resonance (ESR) dating methods (used separately or combined) (Grün et al. 2010; Falguères et al. 2010). However, the main part of diagenetic processes leads to a partial or complete modification of biogenic signal such as elemental or isotopic composition. Uptake of foreign ions such as Strontium, Fluorine, Rare Earth Elements etc. can occur in the first steps of diagenetic processes and continue over geological times (Trueman et al. 2004). The different tooth and bone tissues are more or less resistant to diagenetic alteration. Enamel is considered to be much less sensitive to diagenetic alteration than bone-like tissues (dentin and cement) mainly due to higher crystal perfection and size of its mineral phase, and the very low amount of organic matter.

When the biomineral was transformed into an art object, the alteration phenomena can be different and represent a combination of use wear and diagenetic changes as a function of whether the object was buried or not. Naturally, alterations also occur when the material is extracted from the living tissue. During the life of the animal, the biomineral remains hydrated and this cycle is interrupted when producing the tool or the art object. When the object, for instance an ivory sculpture, has never been buried, the main macroscopic alteration features are cracks induced by changes in humidity and discolorations due to the influence of light.

When the object was buried in stable humid soils, it can be quite well preserved until their excavation in the field. Therefore, the biggest issue of the conservation of buried biomineralised objects is during their excavation. The drying process must be as slow as possible and a high humidity should be maintained as long as possible to avoid bursting. Additionally and also observed on other biological tissues, the alteration features within an object might be variable depending on the environmental conditions and the advancement of alteration (Godfrey et al. 2002; Lafontaine and Wood 1982; Chadefaux and Reiche 2009; Large et al. 2011; Reiche 2011; Reiche et al. 2003, 2010).

Similarly to osseous biominerals, coloured corals and shells, especially red corals that have been used for the decoration of art objects, for instance in the Iron Age, are also subject to alteration processes. During long-term aging of red corals, the calcitic mineral phase is preserved, as it is the most stable calcium carbonate phase under ambient conditions. However, during their burial in the soil, a loss of its intense red colour and shiny surface structure is observed. The degradation processes leading to this fading is probably the degradation of the colorants, e.g. the polyenes that are responsible for the red colour. The altered coral can then be mixed up with other biological materials such as bone, ivory or shell that are light-coloured materials. The fact that corals and other (bio-)minerals were used as small honed studs or pearls (on average only 0.5–1 cm in diameter) makes it even more difficult because there are hardly any distinct surface characteristics of the raw material left. Because such coral decorations are often parts of metallic artefacts, some additional coloured corrosion products from the metal can stain the coral in red or green.

Until now, relatively few studies of the bio-physicochemical alterations have been performed taking into account the different hierarchical length scales of biominerals. Such multi-scale analytical approach combining different complementary methods was recently adapted to determine the preservation state of archaeological elephant ivories and bone. The investigation allowed characterizing both, the mineral and organic phase of ivory, with 2D and 3D structural information on the small samples at all length scales of the hierarchical tissue (Chadefaux and Reiche 2009; Large et al. 2011; Müller and Reiche 2011; Reiche 2009a, 2011; Reiche and Chadefaux 2009; Reiche et al. 2003, 2007, 2010, 2011a; Albéric et al. 2014).

5 Analytical Approaches at Different Length Scales

As mentioned before, structural features and composition of biominerals constitute valuable sources of information in current archaeological records. Many studies have therefore focused on these properties, and various analytical protocols were implemented and used for this purpose (Fig. 7). Archaeological as well as reference materials modified through experimentation (archaeological reproductions) or by artificial aging are studied to understand the observed features and underlying processes at different length scales.

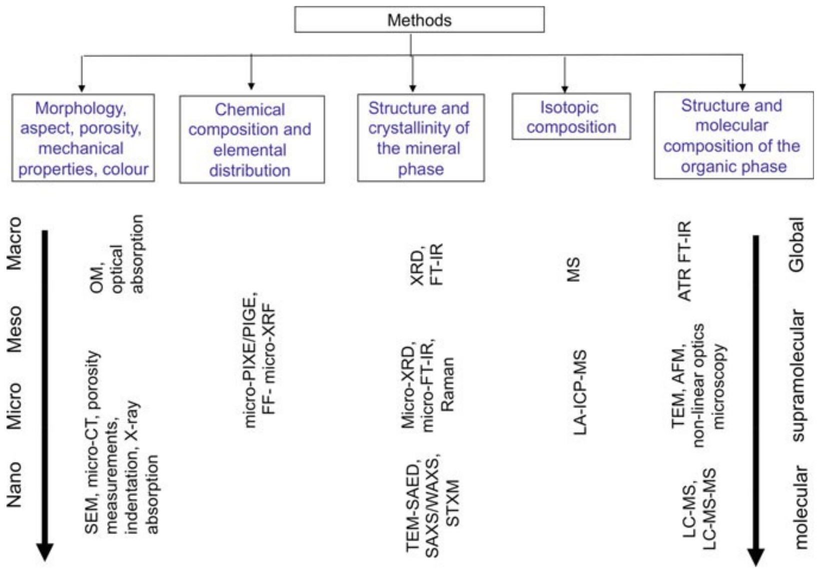

Figure 7 Overview of the generally used analytical techniques for obtaining complementary information on the structure and composition at different length scales of biominerals

Morphological and micro-morphological characteristics of these different kinds of material have been explored by light and electron microscopy (Jans et al. 2002, 2004; Reiche 2009a; Reiche and Chadefaux 2009; Reiche et al. 2003; Turner-Walker and Jans 2008). The organic matter, its structure and content, has been studied by Mass Spectrometry (MS), Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscopy (TEM), etc. (Buckley et al. 2008, 2010; Collins et al. 1995, 1999, 2002; Richter et al. 2011, 2011a; Chadefaux et al. 2009a; Chadefaux and Reiche 2009). Mineral matter composition and structure was investigated by means of X-Ray Diffraction (XRD), FTIR and Raman spectroscopy and various other techniques have been used to screen parameters such as crystallinity, carbonate content or uptake of foreign elements [Sr, F, rare earth elements (REE)] (Person et al. 1995, 1996a; Berna et al. 2004; Rogers and Daniels 2002; Edwards et al. 2006; Edwards and O'Connor 2012; Bartsiokas and Middleton 1992; Trueman et al. 2004, 2008).

Alteration processes enhance the original heterogeneity of these materials at all length scales, and if some parts are well preserved, other ones can be seriously altered. For a long time, most of the techniques were applied to bulk samples studying either the mineral matter or the organic matrix and only a limited amount of data was available on the spatial distribution of present phases in a more or less altered state within such hierarchically structured and composite tissues at different length scales. Since several years, and thanks to the development of new analytical devices with higher performances, site-selective micro- and nano-analyses become available, notably concerning elemental composition and structural features but to a lesser extent concerning isotopic composition (Goodwin et al. 2007; Schweitzer et al.

2008; Reiche et al. 1999; Gaschen et al. 2008; Duval 2011; Fischer et al. 1989). Variations of structural composition at histological scale was not explored until recently on archaeological material, excepted the works by micro- small-angle X-ray scattering (micro-SAXS) of Wess et al. (2001) on archaeological biological material. Recently, new analytical protocols were developed to investigate the composition and structural parameters at micro- and nanoscale by means of TEM on ultrathin sections, 2D FTIR and Raman micro-spectroscopy imaging, by quantitative scanning SAXS imaging (qsSAXSI) and by Full Field 2D chemical imaging using micro-XRF and PIXE (Reiche et al. 2010; Lebon et al. 2011a, b; Bertrand et al., submitted; Gourrier et al. 2007a, 2011b). These methods were developed on modern and experimentally altered (heated) bone samples, and applied to archaeological samples. Particularly, FTIR micro-spectroscopy imaging using synchrotron light was first performed on histological thin sections (<2 μm thick) in transmission mode to investigate qualitatively and quantitatively the mineral (mineral crystallinity, carbonate content, presence of authigenic minerals) and organic phases (collagen alteration state and content) in samples (Lebon et al. 2011a; Reiche et al. 2010). FTIR micro-spectroscopy in Attenuated Total Reflexion (ATR) mode was later applied to be able to analyse hard and brittle samples impossible to cut in very thin sections (Lebon et al. 2016). Quantitative sSAXSI applied on similar samples and TEM on ultrathin sections allows describing texture and crystal size distribution (Gourrier et al. 2011b).

Many of the currently used methods rely on laboratory instruments. One particular case requiring specific developments is the sSAXSI method for the measurement of mineral nanoparticles size, shape, crystal structure and organization. For archaeological bone or dentin for instance, in order to properly take into account the natural and diagenetic heterogeneity, one cannot rely only on traditional atomic or nanoscale sensitive instruments as they fail to provide a sufficient statistical data due to limited fields of view (typically 1–10 μm 2 of a thin section of ~100 nm for TEM). It was recently shown that small- and wide-angle X-ray scattering (SAXS/WAXS), acquired using synchrotron radiation in scanning mode could provide a powerful solution to alleviate this problem in a unique way (Reiche et al. 2014).

The direct coupling of methods such as SAXS/WAXS and Raman, provides a powerful way to characterize archaeological samples since the information are obtained at similar sites and at the sample scale resolution. The organic phase can be analysed on the supramolecular down to the molecular level. The principal organic phase of archaeological biominerals, collagen, can be analysed by FTIR by means of the detection of the amid absorption bands. These bands reflect amid polypeptide groups and the lateral chains of amino acids. The secondary protein structure can also be analysed. Micro-FTIR imaging on thin sections can be used to analyse the organic phase at a histological scale. In addition, analysis of the state of preservation of the organic phase on the level of microscopic fibres can be performed using different kind of microscopies as TEM [50] and Scanning Transmission X-ray Microscopy (STXM) (Benzerara et al. 2006).

The collagen content and distribution on thin sections can also be investigated using Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) (Eriksson et al. 2006). Additionally, as new methodological developments for these purposes, confocal fluorescence and second harmonic generation mode (SHG) microscopies will be used for tubuli and collagen imaging, respectively (Chen et al. 2012; Strupler et al. 2007).

The characterisation of the mechanical properties of biological material is mainly based on indentation experiments. Indentation hardness is used to describe properties of materials such as resistance to penetration and scratching, and rebound resilience; it involves a complex combination of mechanical properties, such as elastic modulus, yield strength, and strain-hardening capacity. It has been shown that microstructure of biological materials influences the indentation hardness and morphology (Cui et al. 1994). As the properties of biological materials presumably depend significantly on its material structure at the micro- and nanometer level, nano-indentation shall be used. Nano-indentation is used to measure small and thin samples. The advantage is that it allows the measure with μm resolution and a depth of penetration up to a few tens of nm.

6 Case Studies

Different case studies are discussed in the following section with the aim to illustrate the different archaeological implications of the study of archaeological biominerals at different hierarchical levels.

6.1 Tracers of Use, Provenance and Circulation of Biominerals in Past Societies

In the following section two examples highlight the approach and the informative potential of biominerals on the use, acquisition and circulation of them in past societies.

6.1.1 Antler Traces Revealed in Palaeolithic Pigments from Lascaux Cave

In numerous research works about a hundred of pigment samples taken in different Palaeolithic cave sites in France and Spain were analysed. Prestigious cave art such as paintings and drawings of Chauvet (30,000 BP), Arcy-sur-Cure (28,000 BP), Lascaux (16,000 BP) and Ekain (Spain) were analysed in order to evidence preparation techniques of painting matter (paint pots) and its way of application. Formula using mineral as “charge” in pigment were brought to the fore (Chalmin et al. 2003). In some of the paint matter, phosphorus and calcium have been found as minor constituents. The presence of this couple of characteristic elements of hydroxylapatite has suggested that crushed bone or antler was used as “charge” to give thickness to painting matter. The use of osseous tools to work the colouring mixture was suggested too.

TEM micrographs (Fig. 8a, b) of two Lascaux pigment samples show, next to the Fe and Mn oxides, Ca and P bearing nanocrystals. The comparison of the crystal features at nanoscale of bone, antler, dentine and the mineral P-containing phase in the Lascaux pigments aims at identifying its nature in the pigment mixture. For this reason, the crystallinity of archaeological and palaeontological bones, dentines and antler was compared by means of different techniques: XRD, FTIR, SEM-EDX and also with PIXE-PIGE and TEM-EDX (Reiche et al. 2002b; Chadefaux et al. 2008a, b). TEM-EDX analysis of the nanocrystals was the method of choice. Besides the investigation of the crystal characteristics, TEM-EDX analysis permits differentiating bone apatite and mineral fluorapatite thanks to the identification of fluorine peak and to quantify the Ca/P ratio.

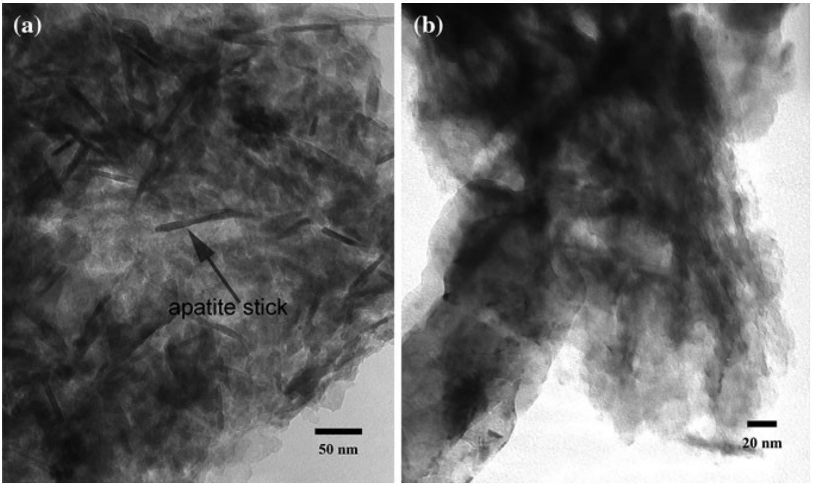

Figure 8 Transmission electron micrographs of two pigment samples a GLAS 62 (brown horse from the "Salle des taureaux") and b 67 (red and black horse from the "Diverticule axial") from the Lascaux cave bearing some apatite sticks possibly originating from antler traces mixed to the pigments. Adapted from Chadefaux et al. (2008a, b)

No significant difference in the chemical composition of altered archaeological bone, reindeer antler or dentine was found. However, crystallinity characterisation shows differences between the features of different archaeological osseous materials at nanoscale. These different features could be used to specify most likely archaeological reindeer antler traces in pigments from Lascaux cave (Chadefaux et al. 2008b). Indeed, sticks with a width of about 7 nm and a length of about 80 nm were observed that show the electron diffraction patterns of apatite. The crystal size is intermediate between modern and very altered reindeer antler found in the Magdalenian reindeer antler fragments. These observations are consistent with the fact that tools made of reindeer antlers were found in the Lascaux cave (Leroi-Gourhan and Allain 1979).

Indeed, the small quantity of calcium and phosphorus measured in the samples may be considered as a pollution, which comes from working the pigments with antler tools. In this case, the fact to find reindeer antler traces in the pigment would not be a deliberate addition by the prehistoric artist to prepare painting matter but more likely pollution. We can imagine that painting and sculpture on bone materials took place in neighbouring or common sites. Nevertheless, the presence of antler in several paint pots allows definiting a "chronological" marker of figures made in a similar period of time. With the absence of absolute dating of the prehistoric figures in the Lascaux cave, this fact give important new possibilities to distinguish the material used for different figures. These markers allow classifying different prehistoric representations and represent also relative chronological marker that can help to decide whether one or several hands painted them in the Lascaux cave.

6.1.2 Identification of the Raw Materials for the Production of Prehistoric Ornaments

The use of biominerals to produce ornaments is a distinctive human behavior that emerges in Europe in the early Upper Palaeolithic (Mellars 1989a, b; White 1995, 2006; Taborin 2004; Vanhaeren et al. 2006; Stiner et al. 2013; Christensen 2004; Christensen and Tejero 2015; Tejero et al. 2012). The exact identification of the raw material used for the manufacture of ancient objects, especially for prehistoric periods, is the basis to get insights into archaeological key questions as availability and circulation of materials, technological capabilities of man in ancient societies, as well as symbolic meanings of the objects. Even if the material identification can, often, easily be made on the basis of macro-morphological characteristics, the identification can be tricky, when the objects are very small or their surfaces have been heavily worked.

This is the case for a specific type of beads excavated from the Final Gravettian level (level 2) of the Abri Pataud (Dordogne, France). Some uncertainty remained about the raw material in which these small beads were made: mammoth ivory,reindeer antler or bone. If ivory could be identified as raw material, the exceptional status of the beads found in Southern France would be emphasized, as ivory is rare among the findings and mammoths didn't live, to our knowledge, in this region at that time period. A large assemblage of body ornaments that consists essentially of 85 quite standardized rectangular beads was found there. Due to their association with the human remains of level 2, these rectangular beads could be considered, like other "extraordinary" objects, as mortuary deposits (Chiotti et al. 2009). Non-invasive methods were employed in order to determine the raw material: microbeam Proton Induced X-ray Emission analysis (micro-PIXE) as well as synchrotron and laboratory X-ray microtomography (micro-CT).

The chemical approach was based on chemical markers for ivory identification, defined thanks to a micro-PIXE database comprising about 150 objects (modern and archaeological ivory, bone and antler) (Müller and Reiche 2011).

However, these chemical markers can be used for the determination of well-preserved objects but cannot be applied for clear identification of diagenetic altered archaeological objects. For this reason, the chemical distinction markers did not enable us to identify the raw material used for the manufacture of the Palaeolithic beads.

Assuming that micro-morphology is less sensitive to diagenetic changes, morphological characteristics for distinction purposes have been studied by means of micro-CT (Reiche et al. 2011b). The micro-CT study allowed establishing distinctive features of modern references of ivory, antler and bone. Tubular pores of about 1–2 μm in diameter are characteristic for ivory, whereas bone and antler show typical osteon structures ranging from 100–500 μm in diameter. Size and shape of the osteons differ between bone and antler and depend strongly on the original localization of the studied sample within the antler. In addition, micro-CT enables the comparison of inner and possibly less altered parts of the objects. By studying archaeological osseous samples from the permafrost as well as determined Palaeolithic fragments from the Abri Pataud, it could be shown that the observed micro-morphological characteristics were preserved even for Palaeolithic diagenetically altered osseous materials. The established parameters were applied on eight beads analysed by synchrotron micro-CT and allowed us to identify ivory for all of them except for one, which shows slightly different morphological features.

The micro-CT analyses confirm that most rectangular beads are made of mammoth ivory. Given the fact that mammoth ivory is rare in level 2 of Abri Pataud, whereas bones and reindeer antler are very abundant, this study demonstrates the exceptional status of this type of beads not only because of their archaeological context, but also due to the choice of raw material for their manufacture (Vercoutère et al. 2011).

6.2 Working Techniques

As illustration of the possible insights that can be gained from studying phosphate-based biominerals, the study of Palaeolithic beads from three French Gravettian key sites in South-western France is discussed here, besides the identification of the used raw material. It will be emphasized that there may be additionally a relationship between shape and function of these body ornaments. A second example of the study of working techniques concerns the study of surface traces of ivory carvings to understand ancient decoration technology.

6.2.1 Insights into the Relationship of the Employed Raw Material, the Shape and the Function of Body Ornaments

The use of biominerals in the production of art and ornaments is a subject of much interest in studies of the Upper Palaeolithic. Material characteristics such as mechanical properties, colour, shape and use-wear are important clues to test hypotheses about the use and symbolic function of Palaeolithic ornaments.

Similar rectangular beads as those found at Abri Pataud (Vercoutère et al. 2011; Chiotti et al. 2014; Reiche et al. 2014) have been discovered in two additional French sites known for the Final Gravettian period: at the rock shelter of Les Peyrugues (Allard et al. 1997; Rodière 2011) and at the site of Le Blot (Chauvière and Fontana 2005). A closer look at these ornaments explains the difficulty of raw material identification and of the study of their use. All beads are relatively small and polished and most of them are varnished today for conservation purposes. The primary feature they share is the central circular perforation. Despite their similarity the beads do show some variation in shape and surface-features. The beads are sometimes rectangular and sometimes more or less oval in outline. They variably show convex and flat surfaces and the presence or absence of incisions next to the central circular perforation. Some of the beads seemed to be made of mammoth ivory, but we couldn't exclude the use of reindeer antler or/and bone, because these raw materials have been previously proposed for the beads found at Les Peyrugues (Allard et al. 1997) and Le Blot (Chauvière 2012; Chauvière and Fontana 2005).

Therefore, a study was devoted to investigate the relationship between the possible use, and status of beads from three key sites of the French Gravettian, through comparative analysis of the raw materials used and morphological characteristics of the beads. A selected set of beads was studied by micro-CT and SEM analysis (Reiche et al. 2014). This analytical approach was also combined with experimentation to simulate the production process. Four steps of the chaine opératoire have been tested: (1) shaping, (2) perforation, (3) segmenting and (4) polishing (Rodière 2011).

Concerning the bead shapes and dimensions, it could be shown that besides a very high degree of standardisation two types of bead can be distinguished: beads with a central symmetric perforation and two convex sides as well as beads with one flat and one convex side presenting an asymmetric perforation combined with a concentric depression surrounding the perforation from the convex side and an incision on the flat side (Fig. 9).

According to first experimental reproductions, the Abri Pataud and Le Blot beads (flat/convex beads) on the one hand have similar dimensions but are different in shape with respect to Les Peyrugues beads (two convex sides) on the other hand. The production process is slightly different although both processes start form a rod. The perforation is produced either symmetrically from both sides (two convex sides) or preferentially from one side (flat/convex beads). Flint tools have been tested and seemed appropriate. This surface could have been gouged out starting from the former shape and reducing its thickness. In both cases the perforation seems to be performed by semi-rotation of ~120°. After the delicate perforation step the beads were cut from the rod and polished, possibly with hematite powder.

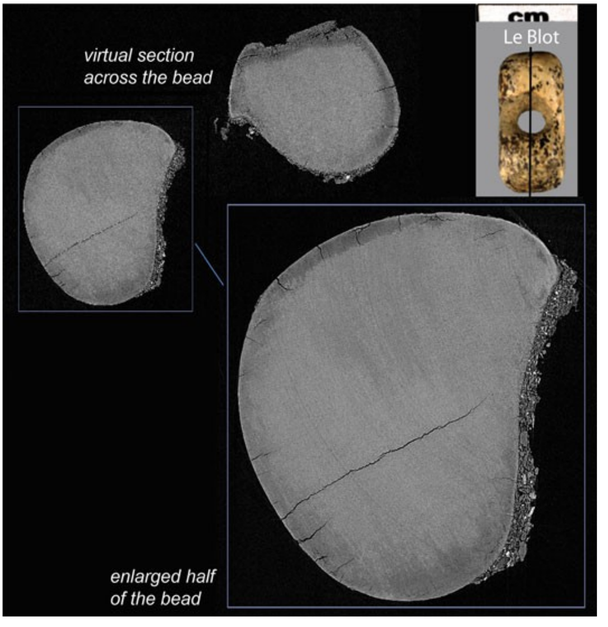

Figure 9 Micro-X-ray CT virtual section of the Gravettian bead from Le Blot site, Dordogne, France

The raw material identification performed by means of micro-CT at the BAMline, at the synchrotron source BESSY II (HZB Berlin, Germany) showed that the bead types defined as a function of their shape corresponds to the classification in terms of the used raw material. The beads with two convex sides are made of antler, possibly reindeer antler, whereas the beads with a convex and a flat side are made of ivory, in the context of mammoth ivory without any exception (Fig. 10). The type of biomineral could be identified thanks to the observation of internal micro-morphological features such as primary Haversian systems for antler and microtubular structure for ivory (Reiche et al. 2011b).

It was, additionally, interesting to check if there may be a relationship between the type of the beads and their usage. If such a relationship was found, it could be indicative of a deliberate choice of raw material for the production of body ornaments with a specific status and function. On the basis of the above mentioned observations two different usages could be hypothesized: (1) the beads with two convex sides could be used for necklaces and (2) the other type with the incision in the flat side could be sewed on clothes. In those cases, antler would be used to produce beads for necklaces while ivory would rather be used for the production of ornaments that were sewed on clothes. Further investigations on more numerous beads including surface and use wear analyses as well as experimental reproductions are necessary in order to confirm these first hypotheses (Reiche et al., accepted).

Figure 10 Examples of two beads from Abri Pataud, Dordogne, France exemplifying the two types of Gravettian rectangular beads observed, left with one flat and one round-shaped side and a preferential perforation from the round shaped side and right with two round-shaped sides and a symmetric bi-perforation

6.2.2 Evidencing Traces of Gilding and Polychromy at the Surface of Phoenician Ivories from Northern Syria (8th c. BC, Syria)

A selection of Phoenician carved ivories excavated at Arslan Tash (Syria), a neo-Assyrian site dating from the 8th century BC, was studied to evaluate the preservation state and to identify the original polychromy. Analogously to neo-Assyrian stone objects, these ivories must have been very colourful (Veri et al. 2009). The objects have been altered due to diagenetic processes during burial, change of environmental conditions when excavated, display and storage in the museums as well as restoration treatments. Today, no visible traces of the original colours are left. The revealing of the original object's appearance is fundamental to better understand the manufacturing technique, the purpose of use for specific objects in order to place them properly in their historical context.

A total of 16 carved ivories of the Département des Antiquités orientales, Musée du Louvre (Paris, France), have been analysed by means of optical microscopy, UV photography, X-ray radiography and micro-PIXE imaging (Fontan and Reiche 2011; Albéric et al. 2015). Additionally, 13 objects kept in the Badische Landesmuseum (Karlsruhe, Germany) could be studied by Full Field Synchrotron micro X-Ray Fluorescence (FF-SR-μXRF) with a new 3D imaging X-ray detector, the Colour X-ray Camera (CXC) at the synchrotron facility ANKA (Karlsruhe, Germany). Full Field-SR-μXRF enabled us to record the elemental distribution of a large area (12.4 × 11.3 mm^2) in 2D elemental maps indicating zones of former coloration (Reiche et al. 2013). The objects are in general well preserved, apart from some cracks, purple stains, black spots correlated to the deposition of MnO_2. The enrichment of several other trace elements (Al, Si, Ti, Fe, Cu, Pb and Au) was detected in respective areas. Al, and Si come surely from sediment residues, but possibly also Ti and Fe. Ti can also refer to restoration treatments. Pb, Cu and Fe can be correlated to pigment residues. Generally, a homogenous distribution of the element ratios may indicate the presence of a former pigment. Over well-defined areas homogeneously distributed Fe and Cu traces in enhanced concentrations were observed and can be considered as pigment residues of the original polychromy (Fig. 11). Iron can presumably be associated to a red pigment (Fe_2O_3) and Cu is likely linked to a blue pigment, copper azurite $2CuCO_3$ as $Cu(OH)_2$ or Egyptian blue containing mainly cuprovivaïte ($CaCuSi_4O_{10}$).

Several objects exhibit two different surface alteration states (well preserved and scratched or rugged surfaces). In all cases the altered area presents increased Cu amounts compared to the well-preserved area. It is thinkable that, the presence of the pigment (and binder) facilitated the deterioration of the ivory surface. The underlying processes remained unexplained so far. The purple stains could be associated with Au traces, probably residues of original gildings. Gold could be identified in the form of nanoparticles (AuNPs).

A detailed study of the possible chemical formation process of AuNPs showed that the collagen originating from the ivory or the glue used to fix the gold on the ivory surface supported the formation of these nanoparticles even at low temperatures through a mechanism implying the formation of hybrid collagen-AuNPs. The collagen stabilizes the dissolved Au ions that form colloids on the nanocrystalline apatite mineral surface of altered ivory. Therefore, these purple stains are indicative of former gilded parts of the carved ivory surface. Additionally, the appearance of such purple stains can be used as a non-invasive authentication criterion, as this process is not yet completely understood and the ancient gilded ivory carvings must have, in principle, been buried for a relatively long time so that the purple stains are formed. Additionally, reproduction seems difficult (Spadavecchia et al. 2014).

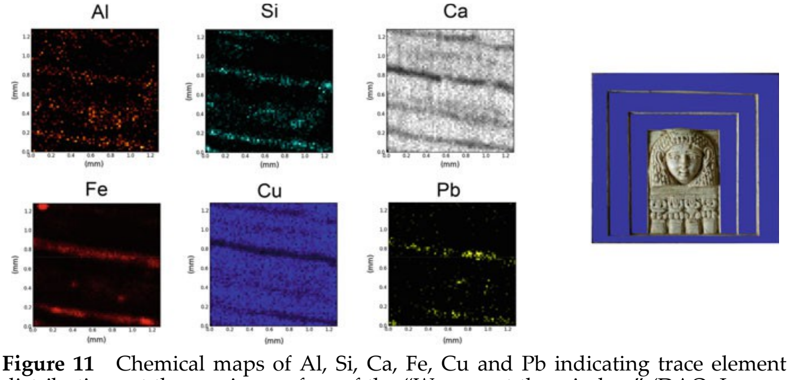

Figure 11 Chemical maps of Al, Si, Ca, Fe, Cu and Pb indicating trace element distributions at the carving surface of the "Woman at the window" (DAO, Louvre museum, Inv. No. AO 11459) allowing the reconstruction of former polychrome decorations. Cu is possibly indicative of *blue* or *green* pigments such as Egyptian *blue* or *green*

6.3 Heat-Induced Transformations

Evidencing unambiguously traces of an intentional heat process is a very important issue in archaeology and prehistory. Therefore, the study of structural markers induced by heat-induced changes at different length scales of the biominerals is crucial for archaeological interpretations of human activities at a given time period. Because of the importance of these questions, the next section is devoted to two studies that highlight the potential information and the analytical difficulties linked with heat-induced transformations of biominerals.

6.3.1 Heat-Induced Changes of Archaeological Bone and Archaeological Implications on the Detection of Fire and Cooking

Traces of heating observed on bone remains and artefacts are often attributed to cremations, cooking, fuel use or naturally occurring fires (Gifford 1981; Weiner and Wagner 1998; Cain 2005; Pijoan et al. 2007; Asmussen 2009; Gonçalves et al 2011). The determination of the heating temperature plays a key role in these studies because it can be related to the kind of heating process. A first (major) complication consists in distinguishing burnt bone from diagenetically altered remains (Nicholson 1996; Shahack-Gross et al. 1997). Secondly, it is important to distinguish intentional heating effects (e.g. due to cooking) from non-intentional ones, which may have occurred following burial (Bennett 1999) or other causes o fire (Asmussen 2009). This implies that even when the observations can unambiguously be attributed to anthropogenic heating effects, it can still be difficult to conclude whether or not the process was intentional. Finally, many subtle anthropological questions require more in-depth analysis, e.g. to distinguish between various modes of heating for cooking (Koon et al. 2003, 2010).

Several qualitative criteria have extensively been used to identify heating temperature and effects: the presence of colour modifications, mass or volume fluctuations and changes in mechanical properties (with respect to modern bone) as an increased brittleness, reduced hardness, presence of fractures (Correia 1996). However, taken individually, such criteria are often insufficient. More holistic approaches need to be considered, taking into account a broad collection of metrics (Thompson 2004). This lead to the derivation of four stages of heat-induced damages roughly corresponding to somewhat overlapping heating temperature ranges (100–600, 300–800, 500–1100 and >700 °C), each stage being associated with specific changes of above mentioned properties (Castillo et al. 2013). From a materials science point of view, this only provides limited insight into the causes and mechanisms leading to bone degradation upon heating. The weakness of such approaches essentially lies in the delicate choice of the parameters used to characterize the heating effects included in the statistical analysis. Clearly, owing to the structural complexity of bone multi-scale analytical approaches from the macroscopic to the nanoscopic scale are required. Moreover, model systems generally need to be analysed in combination with archaeological material to account for possible concomitant diagenetic changes.

Many studies were thus undertaken to clarify this matter by analysing changes in bone structure and properties upon controlled (artificial) heating in, both, field or laboratory conditions using a wide range of characterization methods (Shipman et al. 1984; Holden et al. 1995; Person et al. 1996b; Rogers and Daniels 2002; Piga et al. 2013; Hiller and Wess 2006; Munro et al. 2007; Lebon et al. 2010). A detailed review of the changes observed is beyond the scope of this chapter (see, e.g. Ellingham et al. 2015b) as a wide variety of bones from different human/animal origin and anatomical sites were used. Also, whilst the temperature is always clearly indicated, the heating conditions (duration, heating rate, atmosphere) vary strongly.

Nevertheless a series of rough indications can be derived for dense (cortical) defleshed (but still hydrated) bone samples typically collected from long bones (femur, tibia): the weight loss, mainly associated with the loss of water, increases following a quadratic trend from 5 % w at 100 °C to 30 % w at 300 °C and reaches a plateau of 35–40 % w at 400 °C (Kalsbeek and Richter 2006). This is associated with a progressive denaturation of the collagen followed by degradation at ~400 ° C (Nielsen-Marsh et al. 2000; Bozec and Odlyha 2011) and, consequently, to a significant drop in hardness (Kalsbeek and Richter 2006) and fragility (Stiner et al. 1995). Interestingly, the macroscopic shape and sample histology is found to be relatively well conserved up to ~400 °C, albeit with traces of contamination (ashes and carbon deposition) in the Haversian porosity (Hanson and Cain 2007). In the above mentioned samples, the duration of heating is approximately 1 h and the time necessary to reach the temperature is assumed to be in the order of seconds.

In addition to monitoring collagen changes upon heating at the nanoscale (e.g. using TEM, Richter 1986) and molecular levels [with FTIR spectroscopy (Ellingham et al. 2015a; Lebon et al. 2008; Shahack-Gross et al. 1997; Squires et al. 2011; Thompson et al. 2009, 2011)], many studies were devoted to assess changes in mineral nanocrystal organization (Wess et al. 2002; Hiller et al. 2003; Gourrier et al. 2011a) and crystallographic structure (Person et al. 1996b; Enzo et al. 2007; Rogers et al. 2010; Rogers and Daniels 2002; Piga et al. 2008, 2013). Oddly, while the collagen structure undergoes important denaturation processes before degrading at ~400 °C, a vast majority of experiments point to the quasi-systematic absence of changes in the mineral properties below this temperature. Recently, an extensive combination of physico-chemical analysis showed that there were indeed significant structural changes at those temperatures, most of which occurring at the nanoscale and, thus, difficult to detect (Chadefaux and Reiche 2009). Based on the TEM results, which indicated an increase in nanocrystal size, new measurements were conducted using Synchrotron Small-Angle X-ray Scattering (SAXS) and X-ray Diffraction (XRD) methods. Those new results revealed a two-fold increase in nanocrystal thickness at 300 °C for thin sample sections (100 μm) heated during 1 h (Gourrier et al. 2011a), which confirms previous TEM findings, but contradicts most XRD studies. This showed that SAXS was the most efficient tool to describe the nanocrystal increase in thickness and organization over statistically significant volumes at low heating temperatures (Fig. 12).

An important conclusion to be drawn from this case study: while SAXS had not originally been included in the structural measurement sequence, the multiscale approach adopted by Chadefaux et al. (Chadefaux and Reiche 2009) allowed identifying key markers of heating on bone at the nanoscale. From this global, statistical analysis of fundamental structural parameters (i.e. objective criteria), more appropriate tools were identified (in particular SAXS) to better characterize heat-induced changes at low temperatures. Since many cooking or tool manufacturing procedures could very well fall within this range, this strategy opens new possibilities for related archeological, paleontological and forensic studies.

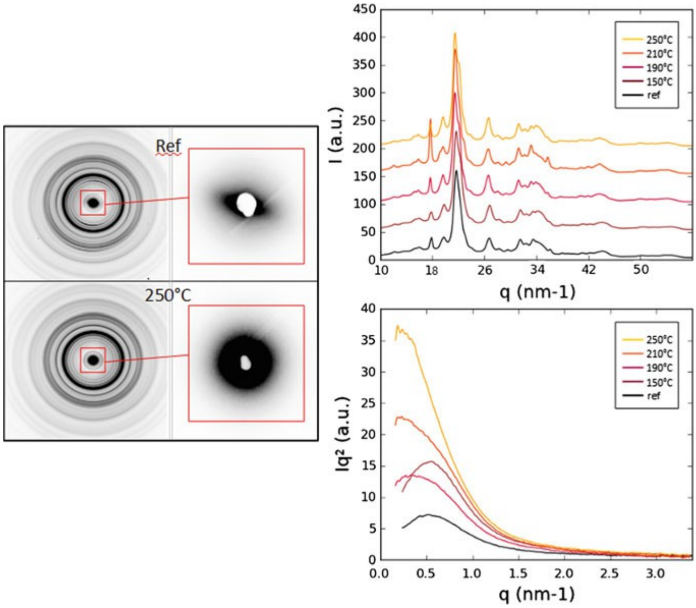

Figure 12 2D XRD pattern (left) of unheated (top) and heated bone at 250 °C (bottom) with the SAXS region show by the corresponding red insets. 1D radial profile of the XRD (center) and SAXS (right) regions as a function of temperature

6.3.2 Evidencing of Accidential or Intentional Heating for Special Techniques of Production of Body Ornaments Made of Shells

The Franchthi Cave is a key archaeological site in Greece with a unique continuous series of archaeological layers spanning from probably earlier than 20,000 years BC to ca 3000 years BC. The prehistoric site is located in the south-eastern Argolid, in a small bay next to the modern Greek village of Koilada, and yielded an exceptionally rich collection of personal ornaments, which belongs to the oldest known in Europe. Excavation at the site began in 1967 and ended in 1976. The deepest sounding in the cave is in Trench F/A (over 11 m of stratified livin debris); the earliest homogeneous cultural deposits yet found (of the Uppe Palaeolithic period) come from Trench H/H1 at a depth of 9 m.

The archaeological reassessment of this category of material culture at the site of Franchthi Cave A performed by Catherine Perlès and Marianne Vanhaeren showed that shells Cyclope Neritea were perforated and were used for the production of body ornaments in the Palaeolithic and Mesolithic period.

The gastropod Cyclope Neritea is a seashell very frequent in the Mediterranean and the Black sea. The shell is living in mudflat on lower cost level. The shell is of about 1 cm in diameter and presents on the dorsal face pastel colours ranging from brown, green to orange and in the ventral face, which is very polished an ivory colour. The composition of the carbonate phase of Cyclope Neritea shell is 98.4 wt % of aragonite with 1.6 % of calcite.

Besides naturally coloured beads, some of the beads showed a dark-brown colour in the archaeological record. This finding led to the hypothesis that one type of personal ornaments, i.e. marine shell beads belonging to the species Cycloperneritea, were intentionally heated to change their natural whitish colour to black. In order to identify possible diagnostic criteria for intentional heating, a small selection of archaeological beads as well as experimental beads were studied. The reference shells were modern Cyclope neritea shells, one of which unmodified, the other experimentally blackened through heating with additional organic material. The two archaeological specimens studied were one presenting a natural whitish colour and another black one. All these beads were submitted to complementary analytical methods: optical (OM) and SEM-EDX, FTIR and micro-Raman spectroscopy as well as Differential Scanning Calorimetry (DSC) in order to identify structural and composition differences of the beads as a function of aging and heat-induced modifications.

Results show that heated black shells can be differentiated based on their microstructure and chemical phases present from the unheated modern and archaeological shells. The modern and archaeological whitish shells are composed of aragonite with some traces of colorant found for the modern white shell. The blackish experimental and archaeological shells in contrast are composed of calcite and present additionally a black C-based compound, namely a compound similar to black graphite as revealed by Raman spectroscopy (Fig. 13). This means that the black archaeological shell positively matches the modern shell blackened through heating. Heating tests showed that the temperatures needed to transform shell aragonite into calcite are relatively low in the range of 280 °C. Identification of the limited conditions meaning in the presence of a large amount of organic matter, in which blackening through heating occurs, further supports a special heat-treatment for Cyclope neritea shells at Franchthi Cave. Indeed reducing atmosphere is needed to produce black carbon remains during the heat process of the shells. The reducing conditions could be obtained by adding organic material such as tree leaves.

This discovery emphasized the fact that the black shells were intentionally heated because special heating conditions needed to be created in order to obtain the wished result of blackening of the shells. Accidental heating would more likely lead to shells with irregular blackening or even a completely whitish colour (Lange et al. 2008; Perlès and Vanhaeren 2010).

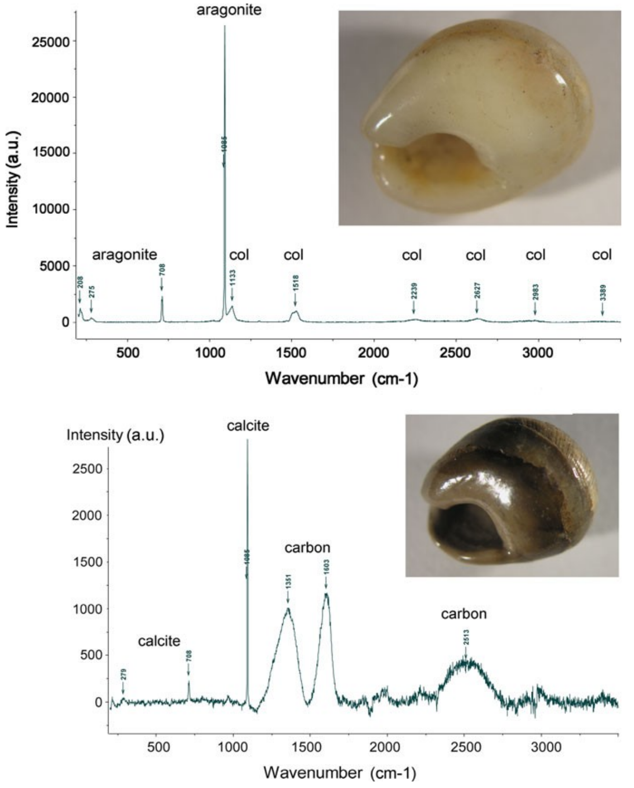

Figure 13 **Figure 12** 2D XRD pattern (left) of unheated (top) and heated bone at 250 °C (bottom) with the SAXS region show by the corresponding red insets. 1D radial profile of the XRD (center) and SAXS (right) regions as a

7 Conclusions and Perspectives

In this chapter the importance of biominerals as archaeological archives wa highlighted. It also emphasized the relevance of considering these highly structure nanocomposite materials at different length scales. Much new information can b gained from their comprehensive study in this way. Particularly invaluable information on ancient working techniques, acquisition and circulation strategies heating and boiling and in general on ancient ways of life can be obtained, I additionally diagenetic and taphonomic changes that can hamper the understanding of these processes, are properly taken into account.

We can benefit from these naturally altered biominerals and use them as a "natural laboratory" to study their durability over time. Such long-term experiments cannot be directly performed in the laboratory and their behaviour upon aging is, at best, approximated under relatively aggressive chemical and physical modifications (e.g.

heating, light, atmospheric gases, cyclic loading etc.). In addition, in the case of archaeological materials, the interplay between the different aging factors is too complex to be analysed in a controlled manner. For the evaluation of the durability of the biominerals, models need to be established, which however never completely reflect the natural or biological conditions. Therefore, archaeological biominerals provide a unique opportunity to study alteration phenomena without applying artificial conditions.

Although archaeological biominerals are precious witnesses of our past, adequate conservation strategies are still lacking. Indeed, they may be sensitive to micro-cracking and powdering for very extreme degradation. As the open porosity of this material is generally very poor, it is very difficult to identify resin formula able to diffuse efficiently in the matrix. The main protocols currently available are usually limited to simple surface treatments. Therefore, there is a real need for designing new practical conservation measures for these materials. Key material features that are beneficial for a good preservation over time could be deduced from these spatially resolved studies and may allow designing new conservation treatments of the archaeological objects as well as inspiring new concepts for modern materials design used in an "archaeo-mimetic" approach.

Indeed, the field of biomimetics studies the engineering of new bio-inspired materials based on the study of biological materials as bone, trees, seashells, sponges, spider silk (Fratzl 2004, 2007). As shown in this chapter nature has developed materials with remarkable properties albeit with a limited set of widely available constituents using different strategies. In a way to make the most of the remarkable properties of biominerals, structure-function relations are very interesting subjects to be studied in detail to be able to use the exceptional properties to design new bio-inspired materials (Fratzl 2007; Currey et al. 1994; Nalla 2003).

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